



# ID Card –Platinum(IV) aqua hydroxo nitrato complexes

(alternative name: 'Platinum dinitrate')

Version 26 September 2019

## Notes:

- This ID card is used to support the substance sameness discussions in SIEFs and to describe the substance to the best of the SIEF members' knowledge.
- It also aims at grouping communications relevant to the request of available data or information, the approval of the proposed Lead Registrant and the registration strategy with the SIEF.
- It is the responsibility of each individual registrant to identify their substance and to report company-specific identity in their Registration Dossier (section 1 of IUCLID).

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## 1. Identification of the substance

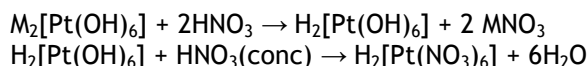
Table 1. Identification of the substance

	New (in EC inventory)	Original (in EC inventory)
Name	Platinum(IV) aqua hydroxo nitrato complexes	Platinum dinitrate
EC number	701-319-4	242-383-9
CAS number		18496-40-7
Description	<p>Platinum(IV) aqua hydroxo nitrato complexes are produced by treating an aqueous solution of Dihydrogen hexachloroplatinic acid with sodium- or potassium hydroxide solution to build corresponding hexahydroxyplatinate (HHP) salt solution:</p> $\text{H}_2\text{PtCl}_6 + 8\text{MOH} \rightarrow \text{M}_2[\text{Pt}(\text{OH})_6] + 6\text{MCl} \text{ with } \text{M} = \text{Na or K}$ <p>Heating of the reaction mixture and an excess MOH is required to drive the reaction to the right and replace the chloride-ligands by hydroxyl-ligands.</p> <p>The solution is washed using e.g. methanol or acetic acid to remove chloride from the system via the formation of a HHP acid precipitate, which is then redissolved in an alkaline sodium- or potassium hydroxide solution to build the HHP salt solution</p> $\text{M}_2[\text{Pt}(\text{OH})_6] + 2\text{CH}_3\text{COOH} \rightarrow \text{H}_2[\text{Pt}(\text{OH})_6]\downarrow + 2\text{CH}_3\text{COOM}$ $\text{H}_2[\text{Pt}(\text{OH})_6] + 2\text{MOH} \rightarrow \text{M}_2[\text{Pt}(\text{OH})_6] + 2\text{H}_2\text{O} \text{ with } \text{M} = \text{Na or K}$	Not available



*Note: removal of chloride is one of the most important properties of the final platinum nitrate solution, in order to prevent corrosion, poisoning and platinum leaching of the heterogeneous catalyst where it will be applied on.*

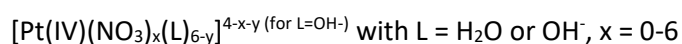
The resulting solution is treated in a first step with nitric acid solution and subsequently with concentrated nitric acid resulting in platinum nitrate solution:



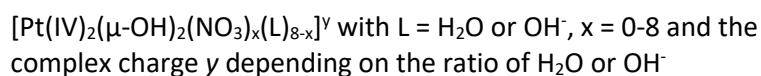
The platinum nitrate solution can be further evaporated to required concentration or to the solid.

Reduction of Pt(IV) to Pt(II) is unlikely due to the strong oxidizing nature of the concentrated nitric acid solution in the final reaction, which has been shown by various authors (Dou et al, 2001; Vasilchenko et al 2018).

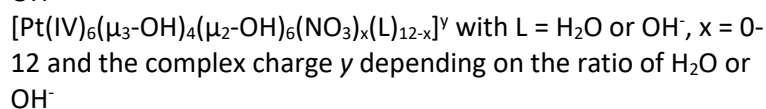
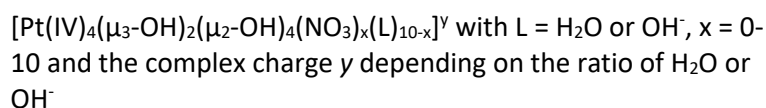
The resulting product contains platinum(IV) species, and the nitrate-ligands might substitute the hydroxyl-ligands. However, it is most likely that mixed mononuclear complexes are formed ('*aquahydroxidonitrato complex*') that can be generically written as:



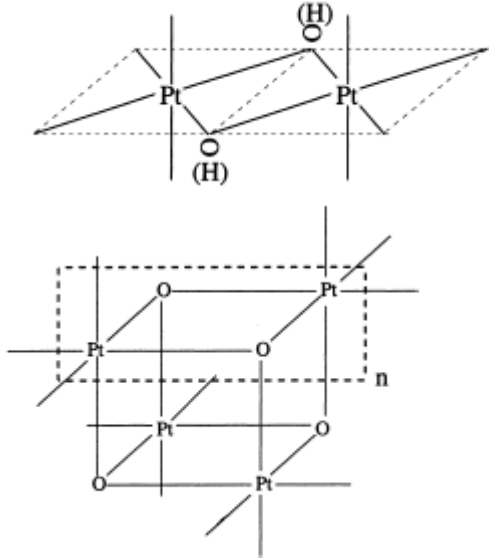
The co-existence of mixed complexes was shown by Vasilchenko et al (2013). When analyzing solutions, and especially solutions that have time to age for a >5 hours, it becomes clear that the  $[\text{Pt}(\text{OH})_6] - \text{HNO}_3 - \text{H}_2\text{O}$  system is very dynamic, and that polynuclear complexes are gradually being formed and become dominant after a few days (Belyaev et al 2011; Venediktov et al 2012; Vasilchenko et al 2013). Octahedral platinum atoms are linked by bridging oxo and/or hydroxyl moieties that can be generically written as:



This primary oligomer structure gives rise to more complex polymer structures like



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	<p>(Dou et al, 2001; Venediktov et al 2012; Vasilchenko et al 2013, 2015, 2018). These can be linear or cyclic complexes (Belyaev et al 2011). This has been generally described in Dou et al (2001) as</p>  <p>Via Pair Distribution Function (PDF) analysis, the structure of the solid Platinum(IV) aqua hydroxo nitrate complexes was confirmed to be as suggested by Vasilchenko et al (2013,2015,2018), and thus similar to generic formula like <math>[Pt_4(NO_3)_{10}(OH)_6]</math> or <math>[Pt_6(NO_3)_{12}(OH)_{10}]</math>.</p> <p>The exact speciation and proportions of the various complexes are unknown, and depend on the exact reaction conditions, storage conditions and age of the product. Because of this undefined polymeric nature of platinum nitrate, this substance has been declared as a UVCB</p>	
Composition type	UVCB	

## 2. Synonyms and other identifiers of the substance

Table 2. Synonyms and other identifiers of the substance

IUPAC name	Platinum(IV) aqua hydroxo nitrate complexes
CAS name	
Abbreviations	None
Other commercial or international names	Platinum(II) nitrate Platinum nitrate Platinum dinitrate Platinum(2+) nitrate Platinum (2+) dinitrate
Other identity codes	



### 3. Substances (with core identifiers) also falling under this substance (with justification)

None

### 4. Typical composition of the substance

The composition given below represents the usual composition available to the Members of the Joint Submission by the date given above on the document. This usual content represents the majority of the Platinum(IV) aqua hydroxo nitrate complexes that is placed on the EEA market.

In a UVCB substance, the number of constituents is relatively large and/or; the composition is, to a significant part, unknown and/or; the variability of composition is relatively large or poorly predictable. Hence, concentration ranges outside the ones given below do not exclude sameness and are usually referred to as unusual or exceptional situations. Each potential registrant is responsible for performing its own analysis.

Table 3 Composition of the solid Platinum(IV) aqua hydroxo nitrate complexesName	Symbol / Formula	Concentration range (%)	Typical concentration (%)
Platinum(IV) aqua hydroxo nitrate complexes		90 - 100 <sup>#</sup>	93
Chloride	Cl	0 - 3	< 0.1
Nitric acid	HNO <sub>3</sub>	0 - 3	1.5
Nitrous acid	HNO <sub>2</sub>	0 - 0.3	< 0.1
Water (residual damp)	H <sub>2</sub> O	0 - 7	5.2
Several minor (especially metallic) constituents which do not affect the classification of the substance because of their non-hazardous nature or because they do not exceed the classification cut-off limits in the substance	e.g. Ag, Au, Cu, Ir, Pd, Rh, Ru	0 - 0,1	< 0.1

<sup>#</sup> Corresponds to 55-61 % Pt

Typical concentration of chloride and nitric acid contents are analytical data. Nitrous acid and water content are calculated from analytical data. Nitrous acid corresponds to content in solution Table 5.

### 5. Information on appearance, physical state and properties of the substance

Table 4. Appearance / physical state / properties of the solid substance

Physical state	Solid
Physical form*	Crystalline
Appearance	Orange to light brown powder
Particle size**	Fine to coarse powder
Does the solid hydrolyse?##	No
Is the solid hygroscopic? <sup>s</sup>	No

\* Crystalline form: solid material whose constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions. Amorphous form: solid material whose constituent atoms, molecules, or ions are randomly arranged.



\*\* Nanoform: particles in the size range 1 - 100 nm (for full definition of a nanomaterial, see <http://ec.europa.eu/environment/chemicals/nanotech/index.htm#definition>). Fine powder: particles in the size range 100 - 2.500 nm. Coarse powder: particles in the size range 2.500 nm - 1 mm. Massive object: particles in the size range > 1 mm.

# Hydrolysis: decomposition (cleavage of chemical bonds) by the addition of water.

§ Hygroscopic substance: readily attracts moisture from its surroundings in open air, through either absorption or adsorption. Cf. also water/moisture content under section 5.

**Table 5. Appearance / physical state / properties of the substance in solution**

Physical state	Solution
Solvent	Water / HNO <sub>2</sub> / HNO <sub>3</sub>
Concentration range of substance in solution	10 - 50 %
pH (range) of the solution	< 1
Excess acid	0 - 3 % HNO <sub>2</sub> 0 - 40 % HNO <sub>3</sub>

## 6. Analytical data

Annex VI of REACH requires the registrant to describe the analytical methods and/or to provide the bibliographical references for the methods used for identification of the substance and, where appropriate, for the identification of impurities and additives. This information should be sufficient to allow the methods to be reproduced.

**Table 6. Analytical methods for identification of the substance**

Parameter / Method	Recommended for substance identification and sameness check	Applicable	Not applicable or not recommended
<b>Elemental analysis</b>			
ICP (ICP-MS or ICP-OES)	X		
Atomic absorption spectroscopy (AAS)			
Glow discharge mass spectrometry (GDMS)			
<b>Molecular analysis</b>			
Infrared (IR) spectroscopy	X		
Raman spectroscopy	X		
<sup>195</sup> Pt NMR spectroscopy	X		
<b>Mineralogical analysis</b>			
X-Ray Fluorescence (XRF)		X	
X-Ray Diffraction (XRD)			
<b>Morphology and particle sizing</b>			
Electron microscopy (SEM, TEM, REM)* #			X
Laser diffraction* #		X	
Particle size by other means (e.g. sieve analysis)#			X
Surface area by N-BET* #		X	
<b>Other</b>			



Gravimetry for Pt content		X	
Total nitrate by ion selective electrode		X	

\* Analytical techniques particularly (but not exclusively) relevant for nanomaterials.

# The choice of the technique for particle size depends on the size of the material as manufactured/imported/placed on the market/used.

## 7. Lead Registrant

Heraeus Deutschland GmbH & Co. KG (Germany) is the Lead Registrant for Platinum(IV) aqua hydroxo nitrate complexes. The EPMF will provide support to the Lead Registrant as laid down in the EPMF Agreement.

## 8. REACH Strategy

The table below presents the overall Registration Strategy for Platinum(IV) aqua hydroxo nitrate complexes based on the information available to the EPMF by the date given above on the document.

The Registration Dossier is prepared for the highest substance status (information requirements associated to a substance or Article 10 Registration being higher than an intermediate handled under strictly controlled conditions or Article 17 or 18 one) and associated tonnage band.

The recap below therefore reflects the scope of work of the EPMF for Platinum(IV) aqua hydroxo nitrate complexes and sets the minimum and maximum set of information that has been gathered and/or produced when preparing the Registration Dossier for Platinum(IV) aqua hydroxo nitrate complexes as described in this ID Card.

If higher information requirements are necessary, these can be included in the Registration dossier (if EPMF is made aware of these additional requirements in-time) as an update to the already submitted dossier.

**Table 7. REACH strategy for the substance (basis for REACH Registration preparation)**

Item	Description
REACH category	UVCB
Highest status	Substance
Highest tonnage band	10-100 t/a
Information requirements	Available / Existing + Annex VII - VIII
Classification	Oxid. Liq 3 (H272) Met. Corr. 1 (H290) Skin Corr. 1A (H314) Eye dam. 1 (H318) Aquatic Acute 1 (H400) Aquatic Chronic 1 (H410)
Registration date	<31 May 2018

## 9. Scope of the Registration Dossier

The uses included in this Registration Dossier are listed on the EPMF website ([www.epmf.be](http://www.epmf.be)).

## 10. Analytical reference information

10.1 Analytical reference information related to the solid Platinum(IV) aqua hydroxo nitrate complexes

IR analysis

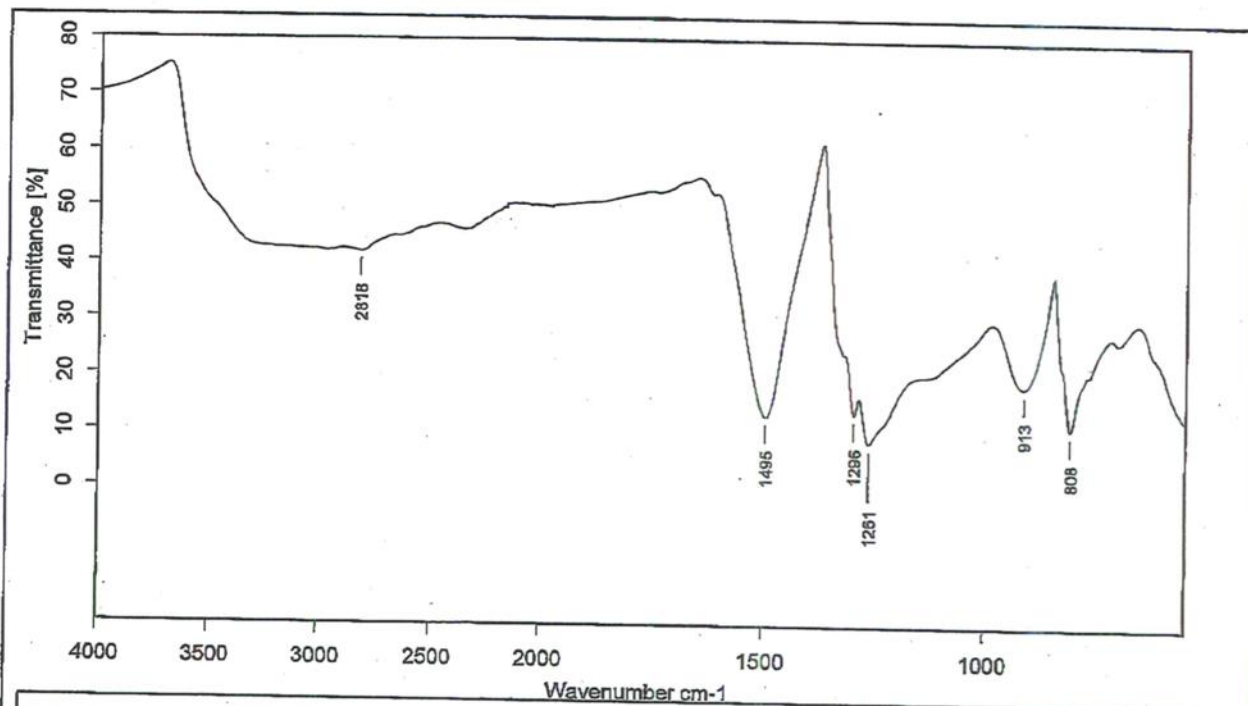


Figure 1. IR spectrum of solid Platinum(IV) aqua hydroxo nitrate complexes

<sup>195</sup>Pt NMR analysis (redissolved solid)

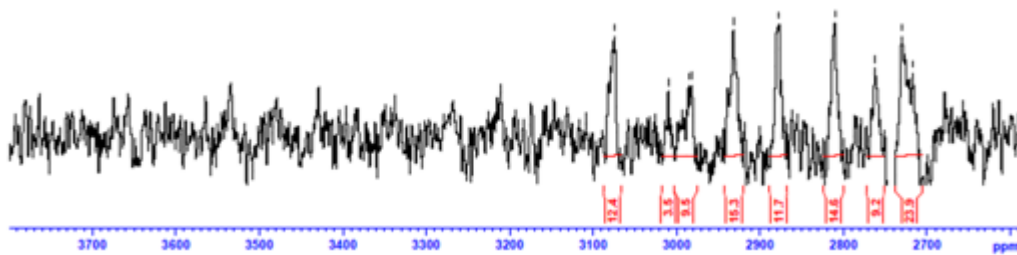


Figure 2. <sup>195</sup>Pt NMR spectrum of redissolved solid Platinum(IV) aqua hydroxo nitrate complexes (redissolved in 32% HNO<sub>3</sub>)

10.2 Analytical reference information related Platinum(IV) aqua hydroxo nitrate complexes in solution

Raman analysis

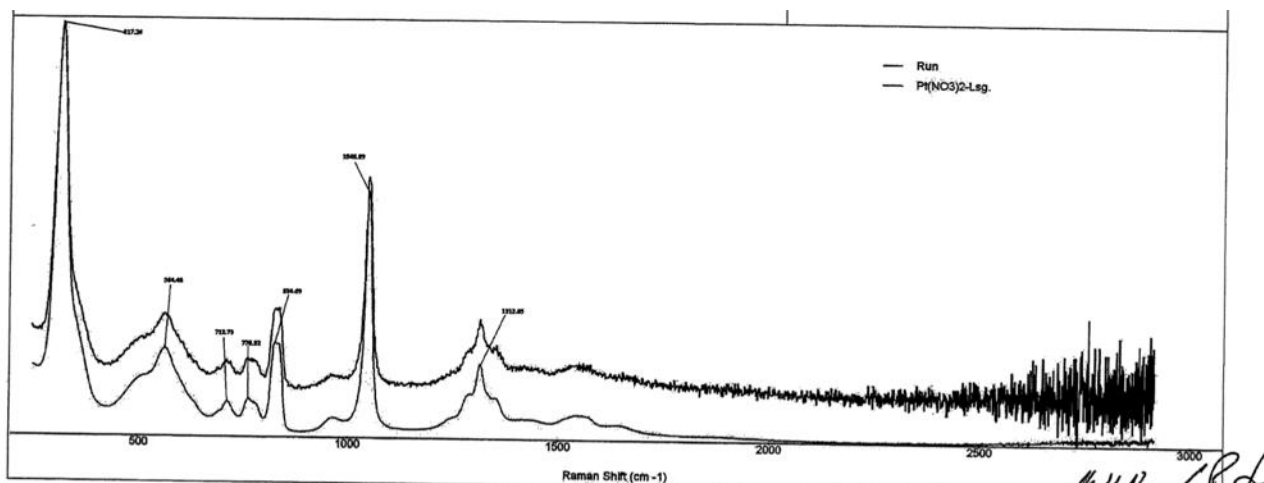
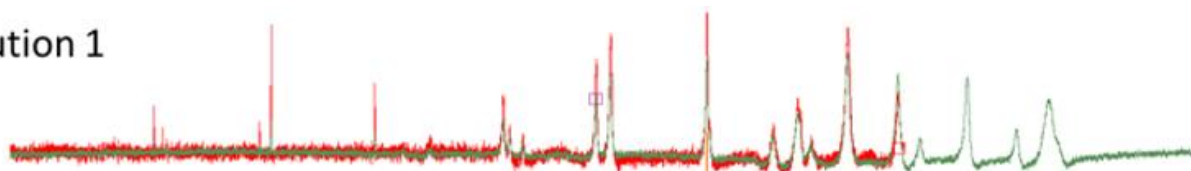


Figure 3. Raman spectrum of Platinum(IV) aqua hydroxo nitrate complexes (in solution)

$^{195}\text{Pt}$  NMR analysis

Solution 1



Solution 2

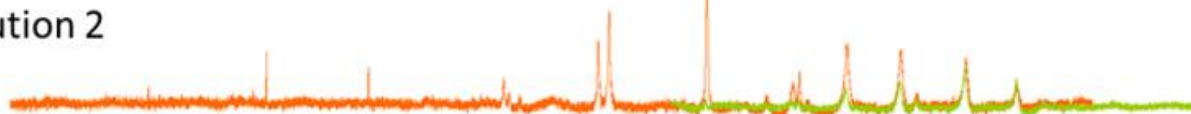


Figure 4.  $^{195}\text{Pt}$  NMR spectrum of Platinum(IV) aqua hydroxo nitrate complexes (in solution)